Anomalous diffusion coefficient in disordered media from NMR relaxation

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Abstract

Application of fractional calculus to the description of anomalous diffusion and relaxation processes in complex media provided one of the most impressive impulses to the development of statistical physics during the last decade. In particular the so-called fractional diffusion equation enabled one to capture the main features of anomalous diffusion. However the price for this achievement is rather high - the fractional diffusion coefficient becomes an involved function of a characteristic of the media (e.g., that of the radius of pores in the case of the porous one). Revealing this dependence from the first principles is one of the main problems in this field of science. Another one still remains that of extracting this dependence from the experiment. The latter problem is tackled in the present paper. Our aim is to provide detailed and pedagogical deriving the relationship of the fractional diffusion coefficient with experimentally observable value from nuclear magnetic resonance (NMR) spin-lattice relaxation data. The result obtained promotes the NMR relaxation method to become a powerful tool in solving the problem of experimental measuring the fractional diffusion coefficient. Also the merits and limitations of NMR relaxation method and pulsed-field gradient (PFG) NMR for the research of anomalous diffusion are compared and discussed.

1 Introduction

Revealing the origin and adequate theoretical description of diffusion and re-
laxation processes have been one of the main concerns for statistical physics
from the very beginning of this field of science. The obstacles that prevent
achieving these aims are augmented substantially with the increase of the
complexity of the system under consideration. That is why the trend to re-
search these processes in the so called complex systems (for review see [1], [2],
[3] and refs. therein) posed new challenges for statistical physics and gave new
impetus to its development. The history of this trend goes back as far as to
the middle of the 19-th century when Kolraush introduced his famous streched
exponential function for the description of charge relaxation in a Leyden gas.
However only the end of the 20-th century is marked by a real breakthrough
and by an explosion of activity in this field of science.

Fractional dynamics is a modern and fruitful approach to the description of
anomalous diffusion processes in randomly disordered media (see [2], [3] and
refs. therein). The idea of this approach goes back to many pioneers whose
achievements are honored in the reviews mentioned above. The reason for
its introducing is as follows. As is well known the mean squared displace-
ment of a free particle in a homogeneous media grows linearly with time

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$< (\mathbf{r} - <\mathbf{r}>)^2 >= 2dC_1t$ where C_1 is the diffusion coefficient with the dimension cm^2/s and d is the (embedding) spatial dimension. This conventional Einstein relationship of the classical theory results from the ordinary diffusion equation for the probability density function to find the particle at position x at time t and is a direct consequence of the Fick's second law. However this simple law does not take place in the inhomogeneous disordered media. The generalization of the Fick's law for complex systems requires conceptually new physical ideas and even envokes to new and rather unusual for common audience mathematics - the so called fractional calculus [4], [5], [6], [1].

One of the basic tools of the fractional dynamics is a fractional diffusion equation (FDE) in which a fractional diffusion coefficient (FDC) C_α with an unusual dimension cm^2/s^α is presented. The case of subdiffusion $(0 < \alpha \leq 1)$ is ubiquitous in nature yielding the mean squared displacement $< (\mathbf{r} - < \mathbf{r} >)^2 >= 2dC_\alpha t^\alpha$ and it originates in any fractal media due to the presence of dead ends on current ways. The FDC acquires a functional dependence on the phenomenological parameter α referring to the extent of inhomogeneity of the system with $\alpha = 1$ corresponding to the case of ordinary diffusion. To establish this dependence for each class of systems is one of the main problems for the theory.

On the other hand the problem has been posed to determine the FDC experimentally. It was pioneered by [7] where the interdiffusion of heavy and light water in a porous media was observed by means of NMR. The authors made use of a one- dimensional form of the FDE and found C_α using the special case of its $\alpha = 2/3$ solution. In [8], [9] the procedure is called "neither very accurate nor of general use". Though such critique may be justified for the particular procedure of the paper [7] one should not think that the abilities of NMR for

measuring FDC are limited somehow. From their own side the authors of [8], [9] proposed a method to measure the FDC with the help of a membrane system where the substance of interest is transported in a solvent from one vessel to another across a thin membrane. In our opinion namely their method is not of general use because it requires the incorporation of a membrane into the system of interest and thus can hardly be applied to, e.g., porous materials. In contrast NMR belongs to non-destructive and non-invasive methods and thus can indeed be of general use. NMR diffusometry [10] is a powerful method for investigation of subdiffusion processes and it is widely applied to exploring transport in porous [10], [11], [12], percolative [13], [14], [7] and polymeric [15] systems. The theory of NMR diffusometry in disordered media [11], [7], [16] is developed within the framework of fractional dynamics [2], [3]. The aim of this chapter is to show how one can retrieve the functional dependence of the FDC on the parameter α from the NMR spin-lattice relaxation data. We obtain a simple analytical formula relating the FDC with the contribution to the spin-lattice relaxation time by anomalous translational diffusion that can in principle be extracted from the experiment.

2 Setting the stage

As is well known in the theory of spin-lattice relaxation by dipole-dipole interaction (see e.g. [17]) the contribution to the spin-lattice relaxation rate constant due to translational diffusion with the spectral density at a Larmor frequency ω_L of the correlation function for spherical harmonics has the form

$$(1/T_1)_{trans} = \frac{3\gamma^4\hbar^2 I(I+1)}{2}\{J^{(1)}(\omega_L) + J^{(2)}(2\omega_L)\} \tag{1}$$

where γ is the gyromagnetic ratio of the nucleus, I is their spin and $\hbar$ is the Planck constant. The spectral densities are proportional to the function $J(\omega)$ of the spectral density

$$J^{(1)}(\omega) = \frac{8\pi}{15} J(\omega) \tag{2}$$

and

$$J^{(2)}(\omega) = \frac{32\pi}{15} J(\omega) \tag{3}$$

Thus the function $J(\omega)$ becomes the key object of the analysis. The consideration of the spin-lattice relaxation in homogeneous media due to diffusion motion of the particles presented in [17] is based on the ordinary diffusion equation for the probability density. To describe the case of inhomogeneous and disordered (e.g., porous) media the generalization of the ordinary diffusion equation within the fractional calculus was suggested by Schneider and Wyss [18] which includes the FDC C_α with the dimension $[\text{cm}^2/\text{s}^\alpha]$. We introduce the characteristic time

$$\tau_\alpha = \left(\frac{d^2}{2C_\alpha} \right)^{1/\alpha} \tag{4}$$

where d is the least distance to which the molecules can approach to each other (if the molecules are considered as spheres of the radius a then $d = 2a$ [17]). For the homogeneous case the normal diffusion coefficient C_1 is given by the Stokes formula

$$C_1 = \frac{k_B T}{6\pi a \eta} \tag{5}$$

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where η the viscosity of the media and consequently the characteristic time is

$$\tau_1 = \frac{12\pi a^3 \eta}{k_B T} \tag{6}$$

The generalization of the ordinary diffusion equation within the fractional calculus suggested by Schneider and Wyss [18] is

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = C_\alpha (D_{0+}^{1-\alpha} \nabla^2 P)(\mathbf{r},t) \tag{7}$$

where $P(\mathbf{r},t)$ is the probability density function to find the particle at position $\mathbf{r}$ at time t, ∇^2 is the three-dimensional Laplace operator, C_α denotes the fractional diffusion constant with the dimension $[\text{cm}^2/\text{s}^\alpha]$ and $D_{0+}^{1-\alpha}$ is the Riemann-Liouville fractional derivative of order $1-\alpha$ and with lower limit $0+$ which is defined via the following relationship [4]

$$\left(D_{0+}^{1-\alpha} f\right)(x) = \frac{1}{\Gamma(\alpha)} \frac{d}{dx} \int_0^x (x-y)^{\alpha-1} f(y) dy \tag{8}$$

where $\Gamma(x)$ is a gamma function. The solution of the equation (7) for the case of sub-diffusion $0 < \alpha \le 1$ with the initial condition $P(\mathbf{r},0) = \delta(\mathbf{r})$ where $\delta(x)$ is a Dirac function is obtained in [18] and expressed via the Fox's function [20], [21], [22]

$$P(\mathbf{r},t) = \frac{1}{(r^2\pi)^{3/2}} H_{12}^{20} \left(\frac{r^2}{4C_\alpha t^\alpha} \left| \begin{array}{c} (1,\alpha) \\ \\ (3/2,1),(1,1) \end{array} \right. \right) \tag{9}$$

The latter is defined as $H_{pq}^{mn}\left(z\left|\begin{array}{c}(a_1, A_1), ..., (a_p, A_p)\\ \\ (b_1, B_1), ..., (b_p, B_p)\end{array}\right.\right) = \frac{1}{2\pi i}\int_L ds z^{-s}\eta(s)$

where $\eta(s) = \frac{\prod_{i=1}^{m}\Gamma(b_i+B_is)\prod_{i=1}^{n}\Gamma(1-a_i-A_is)}{\prod_{i=n+1}^{p}\Gamma(a_i+A_is)\prod_{i=m+1}^{q}\Gamma(1-b_i-B_is)}$. The nomenclature in the Fox's

function associated with the vertical bar is explained via its explicit definition

by the contour integral. The requirements to the contour path L are formu-

lated in [20].

3   Direct problem

In this preliminary Sec. we solve the direct problem - how to calculate the spec-

tral density $J(\omega)$ knowing the FDC C_α ? - and present the detailed derivation

of the result obtained in [16]. We follow the algorithm of [17] (in what follows

all corresponding results from [17] are obtained as a particular case $\alpha=1$ of the

present approach). Under $\mathbf{r}$ we denote the vector $\mathbf{r}_1 - \mathbf{r}_2$ connecting two iden-

tical molecules diffusing relative to each other rather than the radius-vector of

the molecule diffusing relative to a fixed point. This leads only to the change

of $4C_\alpha t^\alpha$ by $8C_\alpha t^\alpha$ in (6). Our aim is to calculate the correlation function

$$G(t) = N\iint \frac{\Upsilon_2^{m*}(\theta(0), \varphi(0))}{r_0^3}\frac{\Upsilon_2^m(\theta(t), \varphi(t))}{r^3}P(\mathbf{r} - \mathbf{r}_0, t)d^3\mathbf{r}_0 d^3\mathbf{r} \qquad (10)$$

where N is the number of spins in 1 cm^3, $\Upsilon_n^m(\theta, \varphi)$ is a spherical harmonic,

$P(\mathbf{r}, t)$ is given by (9) and $*$ denotes complex conjugate. To be more precise

we need the spectral density of the correlation function $G(t)$ to calculate the

spin-lattice relaxation rate constant with the help of (2). At integration in

(10) one should take into account that r and r_0 can not be less than some

limit value d – the least distance to which the molecules can approach to each

other. If the molecules are considered as spheres of the radius a then $d = 2a$ [17].

First we make the Fourier transforming of the function $P(\mathbf{r} - \mathbf{r}_0, t)$ with the mentioned above change of $4C_\alpha t^\alpha$ by $8C_\alpha t^\alpha$

$$
\frac{1}{|\mathbf{r} - \mathbf{r}_0|^3} H_{12}^{20} \left(\frac{(\mathbf{r} - \mathbf{r}_0)^2}{8C_\alpha t^\alpha} \left| \begin{array}{l} (1, \alpha) \\ \\ (3/2, 1), (1, 1) \end{array} \right. \right) =
$$

$$
\frac{1}{(2\pi)^3} \int d^3\mathbf{v} f(\mathbf{v}) \exp\left[i\mathbf{v}(\mathbf{r} - \mathbf{r}_0) \right] \tag{11}
$$

Denoting

$$
\mathbf{R} = \mathbf{r} - \mathbf{r}_0; \qquad\qquad R = |\mathbf{r} - \mathbf{r}_0|; \qquad\qquad v = |\mathbf{v}| \tag{12}
$$

we have the inverse transform (making use of spherical coordinates)

$$
f(v) = \frac{4\pi}{v} \int_0^\infty dR \, \frac{\sin(vR)}{R^2} H_{12}^{20} \left(\frac{R^2}{8C_\alpha t^\alpha} \left| \begin{array}{l} (1, \alpha) \\ \\ (3/2, 1), (1, 1) \end{array} \right. \right) \tag{13}
$$

Substituting (13) into (11), then substituting the result into (10) and making use of the known identities for spherical functions

$$
\int d\Omega \, \Upsilon_l^{p*}(\Omega) \Upsilon_{l'}^{p'}(\Omega) = \delta_{ll'} \delta_{pp'} \tag{14}
$$

$$
\exp(-i\mathbf{v}\mathbf{r}) = 4\pi \left(\frac{\pi}{2vr} \right)^{1/2} \sum_{p,l} i^l \Upsilon_l^{p*}(\Omega) \Upsilon_l^p(\Omega') J_{l+1/2}(vr) \tag{15}
$$

where $J_\nu(x)$ is a Bessel function of order ν we obtain

$$
G(t) = \frac{N}{\pi^{3/2}} \int_0^\infty dv \, f(v) \left[\int_d^\infty dr \, \frac{J_{5/2}(vr)}{r^{3/2}} \right]^2 \tag{16}
$$

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where $f(v)$ is given by (13). Taking the known value of the inner integral

$$\int\limits_{d}^{\infty} dr \, \frac{J_{5/2}(vr)}{r^{3/2}} = v^{1/2}(vd)^{-3/2} J_{3/2}(vd) \tag{17}$$

and denoting $u = vd$ we obtain

$$G(t) = \frac{4N}{\pi^{1/2}d^2} \int\limits_{0}^{\infty} \frac{du}{u^2} \left[J_{\frac{3}{2}}(u) \right]^2 \int\limits_{0}^{\infty} \frac{dR}{R^2} \sin\left(\frac{uR}{d}\right) \times$$

$$H_{12}^{20} \left(\frac{R^2}{8C_\alpha t^\alpha} \, \middle| \, \begin{array}{l} (1, \alpha) \\ \\ (3/2, 1), (1, 1) \end{array} \right) \tag{18}$$

The integration can be fulfilled and yields the expressions for both the correlation function and its spectral density via Fox's functions. However a Fox's function is to regret not tabulated at present either in *Mathematica* or *Maple* or *Matlab*. Thus it is rather difficult to use such formulas for plotting the behavior of the correlation function and the spectral density. That is why it is useful to obtain another representation of the spectral density which enables one to plot the frequency dependence of this function. For this purpose we make the Fourier transforming of the Fox function in (18). The latter can be achieved with the help of the following trick going back to original investigations of Fox. First we make use of (35) from the paper [18] to write

$$H_{12}^{20} \left(\frac{R^2}{8C_\alpha t^\alpha} \, \middle| \, \begin{array}{l} (1, \alpha) \\ \\ (3/2, 1), (1, 1) \end{array} \right) = \frac{1}{2} H_{12}^{20} \left(\frac{Rt^{-\alpha/2}}{(8C_\alpha)^{1/2}} \, \middle| \, \begin{array}{l} (1, \alpha/2) \\ \\ (3/2, 1/2), (1, 1/2) \end{array} \right) \tag{19}$$

Then with the help of transform (57) $\leftrightarrow$ (56) from [19] we obtain

$$
M\left\{\frac{1}{2}H_{12}^{20}\left(\frac{R}{(8C_\alpha\tau_\alpha^\alpha)^{1/2}}\left(\frac{t}{\tau_\alpha}\right)^{-\alpha/2}\left|\begin{array}{l}(1,\alpha/2)\\[1em](3/2,1/2),(1,1/2)\end{array}\right.\right);s\right\}=
$$

$$
\frac{2^{-2s/\alpha}}{\alpha}\left(\frac{2R}{(8C_\alpha\tau_\alpha^\alpha)^{1/2}}\right)^{\frac{2s}{\alpha}}\Gamma\left(\frac{3}{2}-\frac{s}{\alpha}\right)\frac{\Gamma(1-s/\alpha)}{\Gamma(1-s)} \tag{20}
$$

where $M\{...;s\}$ denotes the Mellin transform and τ_α is given by (4). We introduce the designations

$$
x=\frac{t}{\tau_\alpha}; \qquad z=\omega\tau_\alpha; \qquad r=\frac{2R}{(8C_\alpha\tau_\alpha^\alpha)^{1/2}} \tag{21}
$$

and make use of the identity [23]

$$
F_C\{f(x);z\}=M^{-1}\left\{\Gamma(s)\cos\frac{\pi s}{2}M\{f(x);1-s\}\right\} \tag{22}
$$

where F_C denotes the cosine Fourier transform and $M^{-1}\{...\}$ denotes the inverse Mellin transform. Thus for our function of interest

$$
f(x)=H_{12}^{20}\left(\frac{R^2}{8C_\alpha\tau^\alpha}x^{-\alpha}\left|\begin{array}{l}(1,\alpha)\\[1em](3/2,1),(1,1)\end{array}\right.\right) \tag{23}
$$

we have

$$
M\{f(x);1-s\}=\frac{1}{\Gamma(s)\alpha}\left(\frac{r}{2}\right)^{\frac{2(1-s)}{\alpha}}\Gamma\left(\frac{3}{2}-\frac{1}{\alpha}+\frac{s}{\alpha}\right)\Gamma\left(1-\frac{1}{\alpha}+\frac{s}{\alpha}\right) \tag{24}
$$

and

$$
F\{f(x);z\}=2F_C\{f(x);z\}=\frac{2}{\alpha}\left(\frac{r}{2}\right)^{2/\alpha}G(z) \tag{25}
$$

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where

$$G(z) = M^{-1} \left\{ \cos \frac{\pi s}{2} \left(\frac{r}{2} \right)^{-2s/\alpha} \Gamma \left(\frac{3}{2} - \frac{1}{\alpha} + \frac{s}{\alpha} \right) \Gamma \left(1 - \frac{1}{\alpha} + \frac{s}{\alpha} \right) \right\} \qquad (26)$$

The calculation of the inverse Mellin transform in this formula requires routine manipulations with the help of its known properties [24]

$$a^{-s} g(s) \leftrightarrow f(ax); \qquad g(s/h) \leftrightarrow h f(x^h); \qquad \Gamma(s) \leftrightarrow e^{-x}$$

$$g_1(s + A) g_2(s + A + B + 1) \leftrightarrow x^A \int\limits_0^\infty d\xi \; \xi^B f_1(x/\xi) f_2(\xi);$$

$$\sin(\alpha \pi s / 2) \Gamma(s) \leftrightarrow e^{-x \cos(\pi \alpha / 2)} \sin \left(x \sin(\alpha \pi / 2) \right);$$

$\cos(\alpha \pi s / 2) \Gamma(s) \leftrightarrow e^{-x \cos(\pi \alpha / 2)} \cos \left(x \sin(\alpha \pi / 2) \right)$. As a result of tedious but straightforward calculations we obtain

$$G(z) = -\alpha \left(\left(\frac{r}{2} \right)^{2/\alpha} z \right)^{\alpha - 1} \times$$

$$\int\limits_0^\infty d\xi \xi^{-1/2} \exp(-\xi) \exp \left(-\frac{r^2 z^\alpha}{4\xi} \cos \frac{\pi \alpha}{2} \right) \sin \left\{ \frac{r^2 z^\alpha}{4\xi} \sin \frac{\pi \alpha}{2} - \frac{\pi \alpha}{2} \right\} \qquad (27)$$

The substitution of the results into spectral density of the correlation function (10) yields

$$J(\omega) = -\frac{N \tau_\alpha^{1-\alpha}}{\pi^{1/2} d^2 C_\alpha (\omega \tau_\alpha)^{1-\alpha}} \int\limits_0^\infty dR \int\limits_0^\infty \frac{du}{u^2} \left[J_{\frac{3}{2}}(u) \right]^2 \sin \left(\frac{uR}{d} \right) \times$$

$$\int\limits_0^\infty d\xi \xi^{-1/2} \exp(-\xi) \exp \left(-\frac{R^2 (\omega \tau_\alpha)^\alpha}{\xi 8 C_\alpha \tau_\alpha^\alpha} \cos \frac{\pi \alpha}{2} \right) \times$$

$$\sin \left\{ \frac{R^2 (\omega \tau_\alpha)^\alpha}{\xi 8 C_\alpha \tau_\alpha^\alpha} \sin \frac{\pi \alpha}{2} - \frac{\pi \alpha}{2} \right\} \qquad (28)$$

We denote

$$a = \frac{R^2 (\omega \tau_\alpha)^\alpha}{8 C_\alpha \tau_\alpha^\alpha} \sin \frac{\pi \alpha}{2}; \quad b = \frac{\pi \alpha}{2}; \quad c = \frac{R^2 (\omega \tau_\alpha)^\alpha}{8 C_\alpha \tau_\alpha^\alpha} \cos \frac{\pi \alpha}{2}; \quad x = \frac{1}{\xi} \qquad (29)$$

Then the inner integral over ξ is

$$I = \cos b \int_0^\infty dx\; x^{-3/2} \exp\left(-\frac{1}{x}\right) \exp(-cx) \sin(ax) -$$

$$\sin b \int_0^\infty dx\; x^{-3/2} \exp\left(-\frac{1}{x}\right) \exp(-cx) \cos(ax) \tag{30}$$

Both integrals here can be calculated with the help of N2.5.37.2 from [25]. As a result of straightforward manipulations we obtain

$$I = 2g \left(\frac{\pi}{2h}\right)^{1/2} \exp\left(-h \cos\frac{\pi\alpha}{4}\right) \sin\left(h \sin\frac{\pi\alpha}{4} - \frac{\pi\alpha}{2}\right) \tag{31}$$

where

$$g = \left[\frac{R^2(\omega\tau_\alpha)^\alpha}{8C_\alpha\tau_\alpha^\alpha}\right]^{1/4} ; \qquad h = \frac{2R(\omega\tau_\alpha)^{\alpha/2}}{(8C_\alpha\tau_\alpha^\alpha)^{1/2}} \tag{32}$$

We denote

$$B = \frac{2(\omega\tau_\alpha)^{\alpha/2}}{(8C_\alpha\tau_\alpha^\alpha)^{1/2}} \tag{33}$$

The integral over R in (28)

$$K = \int_0^\infty dR\; \sin\left(\frac{uR}{d}\right) \exp\left(-BR \cos\frac{\pi\alpha}{4}\right) \sin\left(BR \sin\frac{\pi\alpha}{4} - \frac{\pi\alpha}{2}\right) \tag{34}$$

after simple manipulations can be cast into the combination of the integrals of the type N2.5.30.8 from [25]. As a result we obtain after straightforward calculations

$$K = -\frac{du^3 \sin\frac{\pi\alpha}{2}}{u^4 + d^2 u^2 \frac{(\omega\tau_\alpha)^\alpha}{C_\alpha\tau_\alpha^\alpha} \cos\frac{\pi\alpha}{2} + \frac{d^4(\omega\tau_\alpha)^{2\alpha}}{4C_\alpha^2\tau_\alpha^{2\alpha}}} \tag{35}$$

Taking into account the definition (4) we finally obtain the formula for spectral density of the correlation function in the general case of inhomogeneus media

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$(0 < \alpha \leq 1)$ [16]

$$J(\omega) = \frac{N\tau_\alpha^{1-\alpha}}{C_\alpha d \left(\omega\tau_\alpha\right)^{1-\alpha}} \sin\frac{\pi\alpha}{2} \int\limits_0^\infty du \left[J_{\frac{3}{2}}(u)\right]^2 \times$$

$$\frac{u}{u^4 + \left(\omega\tau_\alpha\right)^{2\alpha} + 2u^2 \left(\omega\tau_\alpha\right)^\alpha \cos\frac{\pi\alpha}{2}} \tag{36}$$

This formula generalizes that VIII.113 from [17] referring to a particular case $\alpha = 1$ to the case of arbitrary $0 < \alpha \leq 1$. The integration in it can be easily done with the help of *Mathematica* or *Maple* or *Matlab*. Thus this formula is convenient for plotting the spectral density (see [16]). The substitution of this formula into (1),(2),(3) solves the direct problem, i.e., how one can calculate the contribution into spin-lattice relaxation time by anomalous translational diffusion $(1/T_1)_{trans}$ knowing the FDC C_α?

4 Inverse problem

In this central Sec. we tackle some more difficult inverse problem, i.e., how one can calculate the FDC C_α knowing the contribution into spin-lattice relaxation time by anomalous translational diffusion $(1/T_1)_{trans}$? Our solution of this problem is based on the fact that the integral in the (28) can be cast into a form of convolution for Mellin transform $\int_0^\infty \frac{du}{u}\varphi(u)K\left(\frac{x}{u}\right) \leftrightarrow \tilde{\varphi}(s)\tilde{K}(s)$. We factorize the characteristic time into the dimensional part τ_1 ($[\tau_1] = s$) and a dimensionless function $f(\alpha)$ ($f(1) \equiv 1$) accounting for the dependence on the parameter α

$$\tau_\alpha = \tau_1 f(\alpha) \tag{37}$$

The function $f(\alpha)$ plays a key role in our analysis because knowing it we have τ_α and from (4) we obtain the desired value of the FDC C_α. We denote the dimensionless variable

$$x = \omega_L \tau_1 \tag{38}$$

and introduce the function

$$H(x,\alpha) = \frac{5d^3\omega_L}{8\pi N\gamma^4\hbar^2 I(I+1)x}\left(\frac{1}{T_1}\right)_{trans}(x,\alpha) \tag{39}$$

We consider this function as being extracted in principle from the experiment, i.e., as a primarily given one. The condition of normalizing for the function $H(x,1)$ by the requirement $f(1) \equiv 1$ will be given below. Making use of the substitution $u = v^{\alpha/2}$ we obtain from (1) and (36)

$$2xH(x,\alpha) = \alpha\left(f(\alpha)\right)^\alpha \sin\frac{\pi\alpha}{2}\int_0^\infty \frac{dv}{v}\left[J_{\frac{3}{2}}\left(v^{\alpha/2}\right)\right]^2 \times$$

$$\left\{\frac{(x/v)^\alpha}{1+(x/v)^{2\alpha}\left(f(\alpha)\right)^{2\alpha}+2(x/v)^\alpha\left(f(\alpha)\right)^\alpha\cos\frac{\pi\alpha}{2}}+\right.$$

$$\left.\frac{2^{\alpha+1}(x/v)^\alpha}{1+(x/v)^{2\alpha}\left(2f(\alpha)\right)^{2\alpha}+2(x/v)^\alpha\left(2f(\alpha)\right)^\alpha\cos\frac{\pi\alpha}{2}}\right\} \tag{40}$$

Now we apply Mellin transform in the variable x (which we denote $M\{f(x),s\} = g(s)$ or $\leftrightarrow$) to both sides of this equation. Making use of the property $x^\beta f(ax^h) \leftrightarrow h^{-1}a^{-(s+\beta)/h}g[(s+\beta)/h]$ where $a>0$; $h>0$ and of N6.8.33 from [24] we obtain

$$\left[J_{\frac{3}{2}}\left(x^{\alpha/2}\right)\right]^2 \leftrightarrow \frac{2^{2s/\alpha}}{\alpha}\frac{\Gamma\left(1-2s/\alpha\right)\Gamma\left(3/2+s/\alpha\right)}{\Gamma^2\left(1-s/\alpha\right)\Gamma\left(5/2-s/\alpha\right)} \tag{41}$$

where $-3\alpha/2 < Re\ s < \alpha/2$. Making use of N6.2.12 from [24] we obtain

$$\frac{x^\alpha}{1+x^{2\alpha}\left(f(\alpha)\right)^{2\alpha}+2x^\alpha\left(f(\alpha)\right)^\alpha\cos\frac{\pi\alpha}{2}} \leftrightarrow$$

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$$\frac{(f(\alpha))^{-(s+\alpha)}}{\alpha} \frac{\pi \, \sin(\pi s/2)}{\sin(\pi\alpha/2)\sin(\pi s/\alpha)} \tag{42}$$

where $-\alpha < Re \ s < \alpha$. Thus both transforms (41) and (42) have the common region

$$- \alpha < Re \ s < \alpha/2 \tag{43}$$

For (42) to be valid we must be sure that

$$(f(\alpha))^\alpha > 0 \tag{44}$$

To verify the latter we obtain from (4) and (37)

$$(f(\alpha))^\alpha = \left(\frac{2C_1}{d^2}\right)^\alpha \left(\frac{d^2}{2C_\alpha}\right) \tag{45}$$

We see that at C_α be a decreasing function with the decrese of α from the value $\alpha = 1$ (that is an inherent feature of the subdiffusion) the function $(f(\alpha))^\alpha$ is an increasing one from the value $(f(\alpha = 1))^{\alpha=1} = 1$, i.e., indeed (44) takes place.

Applying (41) and (42) to the convolutions in (40) we obtain

$$2M\{xH(x,\alpha), s\} = \frac{2^{2s/\alpha}}{\alpha} \frac{\Gamma\left(1 - 2s/\alpha\right)\Gamma\left(3/2 + s/\alpha\right)}{\Gamma^2\left(1 - s/\alpha\right)\Gamma\left(5/2 - s/\alpha\right)} \times$$

$$\frac{\pi \, (f(\alpha))^{-s}\sin(\pi s/2)\left(1 + 2^{1-s}\right)}{\sin(\pi s/\alpha)} \tag{46}$$

Making use of the properties of a Γ-function we can obtain after straightforward calculations

$$\frac{\Gamma^2\left(1 - s/\alpha\right)\Gamma\left(5/2 - s/\alpha\right)}{\Gamma\left(1 - 2s/\alpha\right)\Gamma\left(3/2 + s/\alpha\right)} = \frac{\pi 2^{4s/\alpha - 1}\left(3/2 - s/\alpha\right)\left(1/2 - s/\alpha\right)}{\left(1/2 + s/\alpha\right)\sin\left(\frac{\pi s}{2}\right)\Gamma\left(2s/\alpha\right)} \tag{47}$$

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Substituting it into (45) we obtain

$$\sin\left(\frac{\pi s}{2}\right)\Gamma\left(2s/\alpha\right)\left(2^{2/\alpha}f(\alpha)\right)^{-s} =$$

$$\alpha M\left\{xH(x,\alpha);s\right\}\frac{(3/2-s/\alpha)\,(1/2-s/\alpha)}{(1/2+s/\alpha)\,(1+2^{1-s})} \tag{48}$$

With the help of N7.3.9 from [24] we obtain

$$\sin\left(\frac{\pi s}{2}\right)\Gamma\left(2s/\alpha\right)\left(2^{2/\alpha}f(\alpha)\right)^{-s} \leftrightarrow$$

$$\frac{\alpha}{2}\exp\left[-2\left(xf(\alpha)\right)^{\alpha/2}\cos\left(\frac{\pi\alpha}{4}\right)\right]\sin\left(2\left(xf(\alpha)\right)^{\alpha/2}\sin\left(\frac{\pi\alpha}{4}\right)\right) \tag{49}$$

where $Re\ s > -\alpha/2$. Thus the common region for all transforms is

$$-\alpha/2 < Re\ s < \alpha/2 \tag{50}$$

Taking the inverse Mellin transform for both sides of (48) we obtain

$$\frac{1}{2}exp\left[-2\left(xf(\alpha)\right)^{\alpha/2}\cos\frac{\pi\alpha}{4}\right]\sin\left[2\left(xf(\alpha)\right)^{\alpha/2}\sin\frac{\pi\alpha}{4}\right] =$$

$$\int\limits_{0}^{\infty}duH(u,\alpha)G\left(\frac{x}{u}\right) \tag{51}$$

where the fuction $G(x)$ is defined as the inverse Mellin transform

$$G(x) \leftrightarrow \frac{(3/2-s/\alpha)\,(1/2-s/\alpha)}{(1/2+s/\alpha)\,(1+2^{1-s})} \tag{52}$$

The poles of its righthand side are $s = -\alpha/2$ and the solutions of the equation $1 + 2^{1-s} = 0$ that are given by $s_m = 1 - \frac{i\pi}{ln2}(2m+1)$ where $m = 0; \pm1; \pm2;\ ....$

Further we consider the case

$$x < 1 \tag{53}$$

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that is sufficient for all practical experimental situations. Then at calculation of the integral

$$G(x) = \frac{1}{2\pi i} \int\limits_{\sigma-i\infty}^{\sigma+i\infty} ds \; x^{-s} \frac{(3/2 - s/\alpha)\,(1/2 - s/\alpha)}{(1/2 + s/\alpha)\,(1 + 2^{1-s})} \tag{54}$$

we can choose $0 < \sigma < 1/2$ and close the contour in the lefthand halfplane (due to (53)). All the poles s_m appear to be beyond its interior and only the pole $s = -\alpha/2$ is inside it. Thus

$$G(x) = res \left\{ x^{-s} \frac{(3/2 - s/\alpha)\,(1/2 - s/\alpha)}{(1/2 + s/\alpha)\,(1 + 2^{1-s})} \right\}_{s=-\alpha/2} = \frac{2x^{\alpha/2}}{1 + 2^{1+\alpha/2}} \tag{55}$$

As a result we obtain

$$exp \left[-2\,(xf(\alpha))^{\alpha/2} \cos\frac{\pi\alpha}{4} \right] \sin \left[2\,(xf(\alpha))^{\alpha/2} \sin\frac{\pi\alpha}{4} \right] =$$

$$\frac{4x^{\alpha/2}}{1 + 2^{1+\alpha/2}} \int\limits_0^\infty du H(u, \alpha) u^{-\alpha/2} \tag{56}$$

This equation implicitly defines the required function $f(\alpha)$ via the given function $H(x, \alpha)$. It is useful to cast it into another form making use of the fact that the left side of this equation has the form of the producing function for a Chebyshev polynom [26]

$$-\sum_{n=1}^\infty \frac{\left(-2\,(xf(\alpha))^{\alpha/2} \right)^n}{n!} U_n \left(\cos\frac{\pi\alpha}{4} \right) =$$

$$\frac{4x^{\alpha/2}}{1 + 2^{1+\alpha/2}} \int\limits_0^\infty du H(u, \alpha) u^{-\alpha/2} \tag{57}$$

Now we take into account that in all practically important situations we can adopt the requirement

$$x << 1 \tag{58}$$

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(e.g., in [16] we had $x = \omega_L \tau_1 = 0.015$). In this case we can restrict ourselves by the first term in the sum only. Taking into account that $U_1 \left(\cos \frac{\pi\alpha}{4} \right) = \sin \frac{\pi\alpha}{4}$ [26] we finally obtain

$$f(\alpha) \approx \left[\frac{2}{\sin \left(\frac{\pi\alpha}{4} \right) \left(1 + 2^{1+\alpha/2} \right)} \int\limits_0^\infty du H(u, \alpha) u^{-\alpha/2} \right]^{2/\alpha} \tag{59}$$

From the requirement $f(1) \equiv 1$ we obtain the condition of normalizing for the function $H(x, 1)$

$$\int\limits_0^\infty du H(u, 1) u^{-1/2} \approx 1 + 2^{-3/2} \tag{60}$$

The desired dependence of the FDC on the parameter α hence has the form

$$C_\alpha \approx C_1 \tau_1^{1-\alpha} \left[\frac{2}{\sin \left(\frac{\pi\alpha}{4} \right) \left(1 + 2^{1+\alpha/2} \right)} \int\limits_0^\infty du H(u, \alpha) u^{-\alpha/2} \right]^{-2} \tag{61}$$

This formula is the central result of this chapter.

5 NMR relaxation or PFG NMR?

As is well known there are two strategies to employ NMR for measuring translational diffusion coefficient: the NMR relaxation method [17] and the PFG NMR (for review see [27], [28] and refs. therein). Both of them have their merits and limitations nicely discussed in [27]. As a matter of fact in the realm of ordinary diffusion the PFG NMR is a fine Prince while the NMR relaxation is a Beggar. However their roles are not so obvious for the case of anomalous diffusion.

The theory of PFG NMR is developed on the base of a combination of Bloch

equations with an ordinary diffusion term pioneered by Torrey [29], [30]. The scheme works well for the case of unrestricted isotropic diffusion but becomes analytically intractable for the case of anisotropic diffusion or that within a confined geometry. While simple geometries are still amenable to analytical approximations more complicated ones require numerical solutions [27]. It is rather problematic to apply this scheme to anomalous diffusion in complex media (in the sense of [1], [2], [3]) where even the geometry as a rule can not be defined.

It is tempting to develop the theory of PFG NMR suitable for the description of the anomalous diffusion along the line of the papers [11], [7], [16] and this chapter. However such a project also encounters severe difficulties. To ehxibit their origin we briefly scetch the mathematical scheme referring for explanation of designations to ,e.g., [30]. In our case instead of (G.7) from [30] we have a fractional Torrey equation

$$
\frac{\partial M^+(\mathbf{r}, t)}{\partial t} = -i\gamma z \left(\frac{\partial H}{\partial z} \right) M^+(\mathbf{r}, t) - \frac{M^+(\mathbf{r}, t)}{T_2} +
$$

$$
C_\alpha (D_{0+}^{1-\alpha} \nabla^2 M^+)(\mathbf{r}, t) \tag{62}
$$

Analogously (G.9) from [30] we seek the solution in the form

$$
M^+(\mathbf{r}, t) = M_0 \exp\left(-\frac{t}{T_2}\right) \exp\left[-i\gamma z \left(\frac{\partial H}{\partial z}\right) t\right] A(t) \tag{63}
$$

Then for the function $A(t)$ we obtain a fractional differential equation

$$
\exp\left(-\frac{t}{T_2}\right) \exp\left[-i\gamma z \left(\frac{\partial H}{\partial z}\right) t\right] \frac{dA(t)}{dt} =
$$

$$
-C_\alpha \left(\gamma \frac{\partial H}{\partial z}\right)^2 D_{0+}^{1-\alpha} \left\{ t^2 \exp\left(-\frac{t}{T_2}\right) \exp\left[-i\gamma z \left(\frac{\partial H}{\partial z}\right) t\right] A(t) \right\} \tag{64}
$$

Recalling the definition of the fractional derivative (8) we can rewrite (64) as an integro-differential equation

$$\exp\left(-\frac{t}{T_2}\right)\exp\left[-i\gamma z\left(\frac{\partial H}{\partial z}\right)t\right]\frac{dA(t)}{dt} = -C_\alpha\left(\gamma\frac{\partial H}{\partial z}\right)^2 \times$$

$$\frac{1}{\Gamma(\alpha)}\frac{d}{dt}\int_0^t ds(t-s)^{\alpha-1}s^2\exp\left(-\frac{s}{T_2}\right)\exp\left[-i\gamma z\left(\frac{\partial H}{\partial z}\right)s\right]A(s) \tag{65}$$

We denote

$$B = C_\alpha\left(\gamma\frac{\partial H}{\partial z}\right)^2 \tag{66}$$

$$c = \frac{1}{T_2} + i\gamma z\left(\frac{\partial H}{\partial z}\right) \tag{67}$$

and make the Laplace transform of (65). Denoting the Laplace transform of the function $A(t)$ as $\beta(p)$

$$A(t) \leftrightarrow \beta(p) \tag{68}$$

we obtain after standard manipulations

$$(p+c)\beta(p+c) - A(0) = -Bp^{1-\alpha}\frac{d^2\beta(p+c)}{dp^2} \tag{69}$$

Introducing a new complex variable

$$z = p + c \tag{70}$$

we obtain an ordinary differential equation

$$B(z-c)^{1-\alpha}\frac{d^2\beta(z)}{dz^2} + z\beta(z) = A(0) \tag{71}$$

The problem we encouter with is to solve the homogeneous part of the equation (71). Introducing a new function $u(z)$ with the help of the relationship

$$\frac{d\beta(z)}{dz} = \beta(z)u(z) \tag{72}$$

we can cast the homogeneous part of the equation (71) into an equivalent form

$$\frac{du(z)}{dz} + u^2(z) = -\frac{z}{B(z-c)^{1-\alpha}} \tag{73}$$

The latter is a Riccati equation. As is well known there is no general way to obtain analytical solution of the Riccati equation and the author of this chapter failed to obtain the solution for our particular case. In our opinion the approach encounters severe mathematical difficulties. We conclude that for the case of anomalous diffusion in complex media the NMR relaxation method has advantage over the PFG NMR because its mathemitical scheme is analytically tractable as the previous Sec. shows. The latter conclusion should be reconsidered because since this Chapter was submitted the problem of fractional Torrey equation has been solved in [31]. In the next Sec. we discuss some difficulties of physical character that still remain and prevent the NMR relaxation method to a become flawlessly accomplished one.

6 Conclusion

As is well known the main problem of the NMR relaxation method is that "the relaxation mechanism of the probe species needs to be known, and it is required that the intermolecular contributions to the relaxation can be separated from the intramolecular contributions" (see [27] and refs. therein). As for the first

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part of the above argument the dipole-dipole relaxation mechanism dominates in very many cases and can be reliably supported upon. However the second part is really a problem. To put it in other words there are contributions to the spin-lattice relaxation rate constant from both translational and rotational diffusion of the tracer molecule

$$(1/T_1) = (1/T_1)_{trans} + (1/T_1)_{rot} \tag{74}$$

The input information for the approach developed in this chapter is $(1/T_1)_{trans}$ and the problem is how to separate it reliably from the rotationl contribution, i.e., to extract it from the experimentally observable value $(1/T_1)$. For the case of ordinary diffusion (both rotational and translational) the problem is solved somehow because we know an explicit expression for $(1/T_1)_{rot}$ [17]. However in a complex media both translational and rotational contributions generally become some functions of the parameter α characterising the extent of inhomogeneity. While the dependence $(1/T_1)_{trans}(\alpha)$ can be calculated explicitly (see [16] and Sec.3 in this chapter) the dependence $(1/T_1)_{rot}(\alpha)$ remains unknown. To develop mathematically the approach for calculation of the latter dependence along the line of [17] basing upon the results of the paper [32] is quite feasible. However a physical problem still remains: whether the parameter α figuring in the fractional derivative of the equation for the translational diffusion should be the same as that for the rotational one? If they differ from each other what is the relationship between them? The author of this chapter does not know the answers to these questions at present. Untill this problem is resolved one should resort to some intuitive physical arguments. In our opinion it seems reasonable to assume that the rotational diffusion depends on the extent of inhomogeneity in a much narrow range than the translational one.

For instance in a porous media the translational diffusion is very sensitive to the radius of the pores in the whole range of this parameter while the rotational diffusion seems to become sensitive to it only when the radius of the pores becomes commensurable with the radius of the tracer molecule. If it is really so then in a wide range of the extent of inhomogeneity $\alpha_c < \alpha \leq 1$ one can assume that $(1/T_1)_{rot}$ is independent of α and use the expression for it from [17] obtained for ordinary rotational diffusion. This trick enanles one to extract the required value $(1/T_1)_{trans}(\alpha)$ from the experimentally observable one $(1/T_1)(\alpha)$

$$(1/T_1)_{trans}(\alpha) = (1/T_1)(\alpha) - (1/T_1)_{rot} \tag{75}$$

The result of such procedure is the input information for the approach developed in this chapter. If it is obtained then the below described strategy is feasible.

The formula (61) relates the FDC with the function $H(x, \alpha)$ (39). The latter takes into account the contribution to the spin-lattice relaxation rate constant by anomalous translational diffusion and can in principle be extracted from the experiment as is described above. Besides α it depends on the dimentionless parameter $x = \omega_L \tau_1$. In practice it is rather problematic to vary the Larmor frequency ω_L. On the other hand the characteristic time (6) $\tau_1 = \frac{12\pi a^3 \eta}{k_B T}$ depends on temperature and can be easily varied during the experiment. This fact enables one to retrieve the dependence of the contribution to the spin-lattice relaxation time due to translational diffusion $(T_1)_{trans}(x, \alpha)$ on x at different α from the experimental measurements. Approximation of the data obtained by a suitable analytical function of two variables yields $H(x, \alpha)$ and substitution of the latter into (61) yields the required dependence of the FDC

on the parameter α.

We conclude that the formula (61) is an ingredient in solving the problem - how to retrieve the fractional the FDC from NMR relaxation data? The mathematical scheme for NMR relaxation method is analytically tractable in contrast to that of PFG NMR. In the latter case the attempts to develop a theory suitable for the description of the anomalous diffusion encouter severe mathematical difficulties. The result obtained in this chapter promotes the NMR relaxation method to become a powerful tool in solving the problem of experimental measuring the fractional diffusion coefficient. However much work still remains to be done for reliable separating the contribution of translational diffusion into the spin-lattice relaxation rate constant from that of rotational diffusion in the experimentally measured values. This preliminary step is necessary for obtaining input information for the approach developed in this chapter.

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